CATALYST LOSS AND RETENTION DURING ALKALI CATALYSED CARBON GASIFICATION IN CO_2

R. Meijer, M. Weeda, F. Kapteijn and J.A. Moulijn

Institute of Chemical Technology, University of Amsterdam
Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Abstract

CO_2-chemisorption appears to be a useful method to characterize alkali-metal-oxide clusters. Although after heat treatment the number of catalytic active sites present on the carbon surface decreases significantly, reactivity and stoichiometry of the sites is not affected by reduction and considerable catalyst loss. The amount of alkali metal that can ultimately be stabilised on the carbon surface during alkali catalysed gasification in CO_2 and heat treatment in helium is primarily dependent on the characteristics of the applied carbon.

Introduction

It is well known that addition of alkali metals to carbonaceous materials has a catalytic effect on gasification. Although the detailed mechanism of catalytic gasification is not completely understood, a generally postulated mechanism [1-5] for catalytic gasification consists of an oxidation-reduction cycle in which oxygen is transferred to the carbon matrix through the active alkali-metal-oxide species (1),(2), followed by decomposition of the oxidised carbon site (3), producing CO. The latter step is generally accepted to be the rate determining step in this process, in which [*] and [O-*] represent the 'empty' and oxygen containing alkali metal species active for oxygen transfer to a free carbon site C_f resulting in a surface oxygen complex C(O).

$$CO_2 + * \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CO + O\text{-}* \qquad (1)$$

$$O\text{-}* + C_f \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C(O) + * \qquad (2)$$

$$C(O) \xrightarrow{k_3} CO + C_f \qquad (3)$$

Kinetic measurements have shown that addition of alkali metal enhances the steady state concentration of C(O) complexes, rather than altering the reaction pathway [3,6,7,8]. In many studies published rates of gasification and oxygen-exchange and results of temperature programmed desorption are related to the initial amount of alkali metal present on the sample [2,9]. By heat treatment (TPD or gasification) catalyst can be lost, the amount being dependent on the alkali metal, temperature and nature of the carbon. Therefore the conclusions of studies that do not account for this effect should be considered with caution.

The amount of alkali metal actually present on the carbon surface is therefore an important parameter in the interpretation of rate, chemisorption and desorption data and understanding of the mechanism of catalysed gasification. Loss of active catalyst can be due to several processes: 1) evaporation of alkali metal (oxide); 2) formation of inactive alkali metal species due to reaction with mineral matter; 3) formation of inactive alkali metal carbonate species; 4) diffusion from the reaction surface into the carbon matrix.

The aim of this study was to examine if and to what extent catalyst loss occurs during potassium catalysed gasification in CO_2 of Norit RX1 Extra samples and how this affects the nature and stoichiometry of the remaining catalytic sites. This was achieved by determination of the potassium content after reactivity measurements, CO_2-chemisorption and temperature programmed desorption. The properties of the carbon have been varied by pretreatment in an inert atmosphere (Ar) at temperatures up to 2000 K.

Experimental

I. *Sample preparation*

The activated carbon used in this study is Norit RX1 Extra, an acid washed, steam activated peat char with a high specific surface area (1100 $m^2.g^{-1}$ (CO_2(DR),273 K), 1500 $m^2.g^{-1}$ (N_2(BET),77 K), d_p = 0.25−0.6 mm). Addition of catalyst (0−20 wt% K_2CO_3) to fresh and heat treated (up to 2000 K in argon) carbon samples was performed by pore volume impregnation with an aqueous solution. The initial catalyst loading is expressed as the atomic potassium to carbon $(K/C)_i$ ratio. The alkali metal content was determined (in duplo) by Inductive Coupled Plasma Atomic Emission Spectroscopy (ICP−AES), after acid washing of the samples (2% HNO_3).

II. *Apparati*

The data obtained in this study were generated in a Fixed−Bed flow Reactor (FBR). Experiments in a thermobalance (SETARAM TG 85) were performed for monitoring weight changes during CO_2−chemisorption, Temperature−Programmed−Desorption (TPD) and gasification experiments.

Basically the FBR apparatus [10] consists of two gas mixing sections in which the desired gas mixture can be generated, an oven (T_{max} = 1273 K) containing the carbon sample in a quartz reactor (I.D. = 3 − 5 mm , P_{max} = 0.15 MPa) and a GC (He carrier, TCD detection) and MS (Leybold−Heraeus Q200) for gas analysis. All gases used are of HP or UHP grade and are purified (O_2 and/or H_2O removal) before they are fed to the reactor.

III. *Experimental procedure*

In this study two experimental schemes were applied (figure 1). Resulting in the following seven different procedures (stages between brackets are optional):

type	treatment
1a	SSG
1b	SSG − TPD − SSG
1c	SSG − CO_2-chem. − TPD
1d	SSG − [CO_2-chem.] − TPD − CO_2-chem. − TPD
2a	TPD
2b	TPD − SSG − [TPD]
2c	TPD − CO_2-chem. − TPD

The first step in each experiment was drying *in situ* (T = 473 K, He) of the catalyst/carbon sample (50−100 mg). Partial gasification of the catalyst/carbon sample was performed in 20 μmol $CO_2.s^{-1}$ (T = 1000 K ; P = 0.12 MPa). The steady state gasification rate (SSG) in the FBR is based on either the actual amount of potassium (r_K) or the initial amount of carbon (r_n) present, and expressed as (μmol carbon gasified).(μmol K_a or C_i)$^{-1}$.s^{-1}.

TPD patterns in the FBR are obtained in a flow of 20 μmol $He.s^{-1}$ with a heating rate of 10 $K.min^{-1}$ up to 1200 K, followed by an isothermal period of 30 minutes at 1200 K. The amount of CO and CO_2 released expressed as (μmol CO_x desorbed).(μmol K actually present)$^{-1}$.s^{-1} is plotted as a function of temperature.

After partial (approximately 25% burn−off) gasification in CO_2 (type 1 experiments) the sample was exposed to helium at 1000 K and cooled to 673 K followed by either TPD and gasification (type 1b), CO_2−chemisorption and TPD (type 1c), or a second CO_2−chemisorption and TPD cycle (type 1d).

After TPD of a fresh sample (type 2 experiments) the sample was cooled to either room temperature for potassium analysis (type 2a), to 673−873 K for CO_2−chemisorption (type 2b) or 1000 K for gasification (type 2c), followed by a second TPD.

At the end of each experiment the sample was cooled to room temperature and the potassium content of the residue was determined. The potassium could be quantitatively recovered from the catalyst/carbon residue with an aqueous 2% HNO_3 solution.

Results

Gasification reactivity vs catalyst loading.

The steady state gasification rate for fresh and residual K_2CO_3/Norit RX1 samples is shown in figure 2. For fresh samples (open symbols) the observed gasification rate r_K at 25% burn−off clearly shows a constant value at $(K/C)_a > 0.02$. Over this K/C range investigated the activity per potassium atom is constant. The observed gasification rate r_K of residual samples (closed symbols), independent of the initial loading, corresponds well with rates of fresh samples. Clearly the reactivity per K atom is not affected by extensive potassium loss and repeated heat treatments up to 1200 K.

Figure 3 gives the fraction of catalyst still present as a function of burn−off for samples with different initial potassium loading. It was found that already at low burn−off about 20 to 40 % of the potassium is lost, independent of the initial catalyst loading. This amount remains further fairly constant over the burn−off range investigated (0−60%).

In figure 4 the K/C ratio based on the K actually present (ICP−AES values) is plotted as a function of the K/C ratio calculated from the amount of K initially added. Clearly during TPD extensive potassium loss takes place. During a second heat treatment up to 1200 K no extensive additional catalyst loss occurs. The results show that the amount of alkali metal that can be stabilised on the carbon surface (K/C = 0.018−0.02) during TPD up to 1200 K is nearly independent on the initial alkali metal loading. Furthermore, the amount of alkali metal that ultimately can be stabilised on the carbon surface is strongly affected by the temperature at which the carbon sample has been pretreated (K/C ≃ 0.007 ; $T_{pretreat}$ = 1650−2000 K).

Thermogravimetric measurements show that the amount of oxygen present in the carbon sample decreases with increasing heat treatment temperature.

Outgassing patterns

TPD patterns of fresh carbon/catalyst samples (type 2a,2b,2c) are very reproducible and are fairly similar for all samples investigated. They exhibit a low temperature (400 − 950 K) CO_2 desorption, followed by a two peak CO desorption. The first CO desorption is due to gasification of desorbed CO_2 [11], while the second is ascribed to decomposition of phenolate groups [7,11,12,13,14], the anchors for the alkali−metal−oxide clusters active for alkali catalysed gasification. TPD patterns obtained after gasification in CO_2 at 1000 K and subsequent cooling in helium show only one CO peak. In general the maximum CO desorption shifts to lower temperature with increasing alkali metal loading and the CO/K_a desorption ratio decreases in the same order.

In figure 5a TPD patterns are shown after SSG followed by CO_2−chemisorption at 673 K. The low temperature CO_2−desorption is associated with this CO_2−chemisorption, whereas the high temperature CO desorption is similar as obtained from a TPD after SSG without chemisorption.

TPD patterns after TPD and CO_2−chemisorption at 673 K (type 1d,2c) also show low temperature CO_2 desorption from the alkali metal cluster (figure 5b). The amount of CO or CO_2 desorbed has been corrected for potassium loss during the first TPD. From figure 5b it is clear that independent of the initial potassium loading the TPD patterns are comparable, since the amount of potassium present during this second TPD is about the same for all three samples. However the amount of CO desorbed per K atom present (0.3−0.4) during this TPD (figure 5b) is considerably lower than in a TPD after gasification (0.9, figure 5a).

In figure 6 the outgassing patterns of differently treated samples are compared. A fresh sample shows extensive low temperature CO_2 desorption and only a small amount of high temperature CO desorption. If CO_2−chemisorption is performed at 873 K the total amount of CO/K_a desorbed increases significantly compared with CO_2−chemisorption at 673 K, approaching the CO/K_a ratio desorbed after partial (25% burn−off) gasification at 1000 K (CO/K_a= 0.9). The maximum CO desorption shifts to a temperature comparable to that of desorption of phenolate like species. The amount of CO_2/K_a desorbed decreases with increasing chemisorption temperature (0.33 → 0.22).

Experiments performed in the thermobalance with catalyst/carbon samples show an instantaneous weight increase on CO_2 introduction at 673 K, corresponding to a CO_2/K_a ratio of approximately 0.3, which is in agreement with the TPD results. Pure carbon shows no weight change, thus the assumption that the weight increase can be attributed to CO_2 in the alkali−metal−oxide cluster is justified.

Discussion

The fact that during alkali catalysed gasification, using pore volume impregnated catalyst/carbon samples, catalyst loss at low burn−off is substantial (figure 3) was also found by Sulimma et al. [15] in the case of steam gasification. They furthermore observed a substantial increase in catalyst loss with increasing burn−off.

Our results concerning the amount of alkali metal that can ultimately be stabilised by the carbon surface are consistent with results reported in literature. Shadman et al. [16] reported K/C = 0.002 after complete reduction in nitrogen at 1073 K for an alkali−carbonate/Carbopack B sample (graphitized carbon , S_a = 100 $m^2.g^{-1}$).

The fact that potassium shows interaction with the carbon, resulting in an amount that can be stabilised on the carbon at high temperature was already observed by Tromp and Cordfuncke [17]. They also concluded that pretreatment of a catalyst/activated carbon sample at higher temperature resulted in an decrease in alkali carbon interaction. Saber et al. [18] concluded that after heat treatment in an inert atmosphere at 1350 K the amount of potassium loss by volatilization increases with decreasing oxygen content of the carbon. This is consistent with our data which show that after heat treatment of the carbon sample (1650−2000 K) the K/C ratio that can ultimately be stabilised by the carbon surface at 1200 K is considerably lower than for unpretreated samples (K/C = 0.007 vs. 0.018).

Gasification of K_2CO_3/Norit RX1 residues which have undergone considerable catalyst loss, shows that the observed gasification rate per μmol potassium present (r_K) is similar to that of fresh samples with the same $(K/C)_a$ ratio. Sams et al. [19] concluded that independent of initial loading and heat treatment time the rate is an unique function of the $(K/C)_a$ ratio with the restriction that the K/C value is below the saturation level.

The percentage and rate of potassium loss during alkali catalysed gasification or heat treatment in an inert atmosphere reported in literature differ enormously [8,14,15,16,18,19]. The amount of alkali metal that can ultimately be stabilised on the carbon surface is dependent on the characteristics of the applied carbon (oxygen content and heat treatment temperature). The rate at which potassium is lost is however strongly dependent on the experimental conditions (apparatus, *T*, *P*, flow rate, gas phase) and the method of impregnation [15].

Outgassing patterns

TPD patterns of fresh and partial gasified alkali−carbonate/Norit RX1 Extra samples are in good agreement with earlier reported patterns by Kapteijn et al. [11]. From figure 5a it can be seen that CO_2−chemisorption at 673 K after partial gasification produces the same CO desorption pattern as with direct outgassing after gasification. Samples with different initial catalyst loading still show distinct differences in outgassing pattern. A second outgassing with the same sample (figure 5b) shows that, as expected from the alkali metal measurements, the CO_2 and CO outgassing patterns have become rather independent of the initial catalyst loading; it is also clear that the amount of CO desorbed (CO/K_a = 0.3−0.4) is considerably lower than after gasification or CO_2−chemisorption at 873 K (CO/K_a = 0.9).

CO_2−chemisorption after TPD shows a distinct difference in CO desorption pattern with increasing chemisorption temperature (figure 6). From the absence of high temperature CO desorption it is concluded that at low CO_2−chemisorption temperature (673 K) it is not possible to restore all catalytic sites active for gasification. This indicates that, although CO_2 is chemisorbed at 673 K inside the alkali−metal−oxide cluster, only a small amount of oxygen is built in with direct interaction with the carbon. Ratcliffe [12] showed that on outgassing of a K_2CO_3/Spherocarb sample after $^{13}CO_2$−chemisorption at 333 K , ^{13}CO desorption as a result of $^{13}CO_2 + C_f \longrightarrow {}^{13}CO + C(O)$ was detected between 700 and 800 K. This ^{13}CO desorption was followed at higher temperature by ^{12}CO release, with a maximum at 1030 K due to desorption of the oxidized carbon sites. This was also reported by Kelemen and Freund [8] and corresponds to the outgassing patterns in figure 5b in which clearly two ^{12}CO desorption peaks can be observed. The first is due to decomposition of chemisorbed CO_2, the second can be described to two processes: a minor desorption of oxidised carbon sites ($C(O) \rightarrow CO$), and a major decomposition of 'phenolate' groups ($C-O-K \rightarrow CO + K$), being the anchors for the catalytic active alkali−metal−oxide species.

Although CO_2−chemisorption at 673 K after TPD shows a low CO/K_a ratio (±0.3) the same CO_2/K_a ratio (±0.3) is found as after gasification.

These values are in good agreement with CO_2-chemisorption results reported by Mims and Pabst [4], Ratcliffe and Vaughn [13], Cerfontain [20] and Koenig [21], indicating that the alkali metal cluster even after reduction and considerable catalyst loss, can chemisorb one CO_2 molecule per every 3 to 4 potassium present on the surface.

Conclusions

The most important conclusions that arise from this study are:

* The amount of potassium that can ultimately be stabilised on the carbon surface is primarily dependent on the oxygen content of the carbon. This can be reduced by heat treatment of the applied carbon.
* Although the number of active sites present on the carbon surface decreases significantly during TPD or gasification, the intrinsic reactivity and stoichiometry of the sites under gasification conditions is not affected.
* CO_2-chemisorption below 700 to 800 K is not capable of completely restoring the 'phenolate' groups that act as the anchors of the catalytic active alkali-metal-oxide sites. Above this temperature clearly these groups are formed.
* The catalytic active potassium (oxide) cluster is capable of chemisorbing one CO_2 molecule per every 3 to 4 potassium atoms present. This seems to be generally valid.

Acknowledgement

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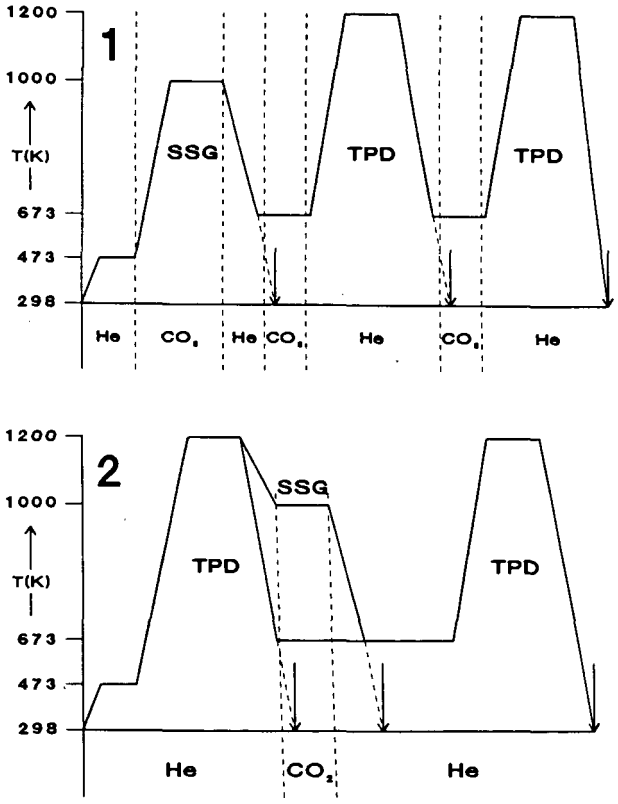


Figure 1 : Experimental procedures: type 1 (upper part) and type 2 (lower part). SSG and TPD refer to Steady State Gasification and Temperature Programmed Desorption.
The arrows indicate the points in the experiments at which alkali metal determinations were performed.

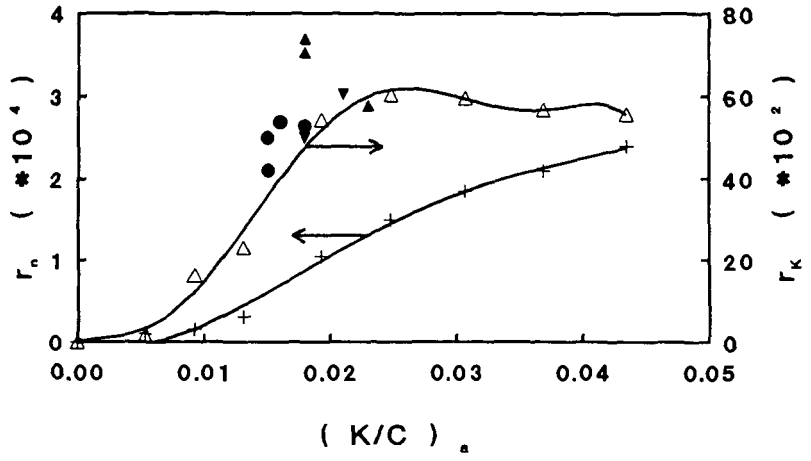


Figure 2 : Steady state gasification rate (T=1000 K, P=0.12 MPa) of fresh (open symbols) and residual (closed symbols) K_2CO_3/Norit RX1 samples as a function of the actual K/C ratio (+ - r_n ; △ - r_K ; ● $(K/C)_{initial}$ = 0.019; ▼ $(K/C)_{initial}$ = 0.031; ▲ $(K/C)_{initial}$ = 0.043).

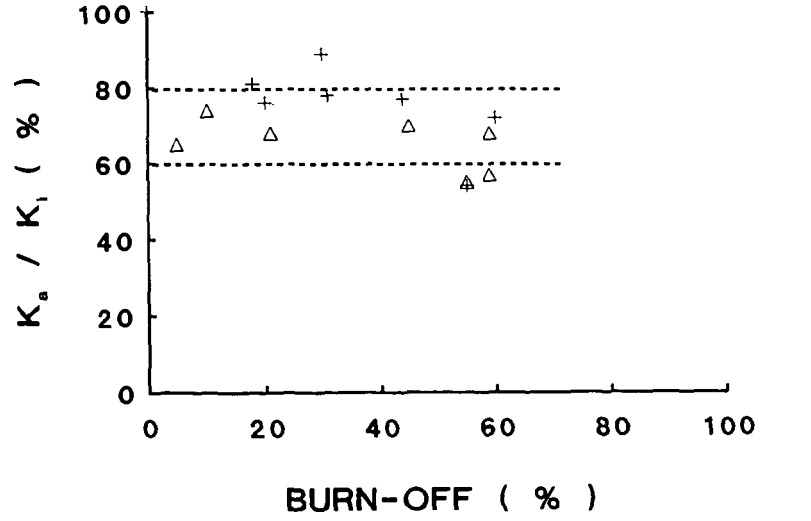
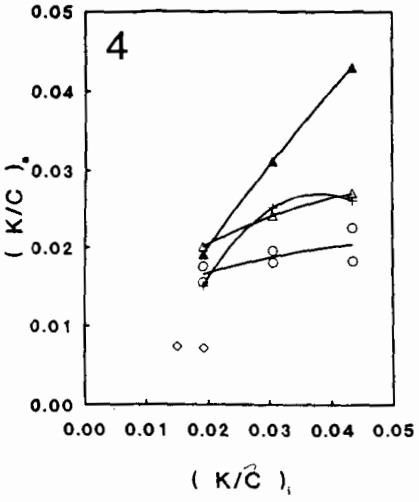
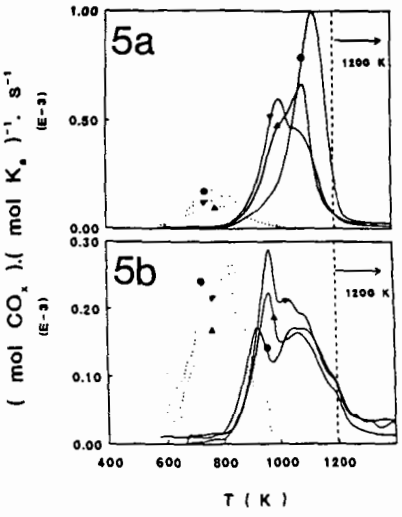


Figure 3 : Catalyst loss (K_a/K_i)as a function of burn-off during alkali catalysed gasification in CO_2 (T=1000 K, P=0.12 MPa).
+ $(K/C)_{initial}$ = 0.019
△ various loadings: $(K/C)_{initial}$ = 0.0054 - 0.0435





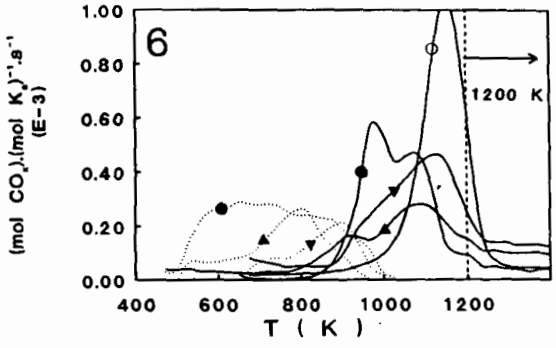


Figure 4 : Actual (K/C) ratio as a function of the initial (K/C) ratio after different treatment: ▲ no treatment; + TPD; △ SSG and TPD; ○ second TPD; ◇ TPD heat treated carbon samples.

Figure 5 : First(5a) and second(5b) TPD patterns after CO_2-chemisorption at 673 K (type 1d experiment) of samples with varying initial potassium loading. (----- = CO_2 ; ——— = CO ; ● $(K/C)_{initial}$ = 0.019 ; ▼ $(K/C)_{initial}$ = 0.031 ; ▲ $(K/C)_{initial}$ = 0.043)

Figure 6 : TPD patterns for K_2CO_3/Norit RX1 Extra $(K/C)_{initial}$ = 0.019 samples (---- = CO_2 ; ——— = CO).
- ● fresh sample
- ▲ after TPD and CO_2-chemisorption at 673 K
- ▼ after TPD and CO_2-chemisorption at 873 K
- ○ after partial gasification (CO_2 , 1000 K) to approximately 25 % burn-off.